



**U.S. Department of Energy**  
**Office of River Protection**

P.O. Box 450, MSIN H6-60  
Richland, Washington 99352

12-TF-0009

MAY 02 2012

Ms. Jane A. Hedges, Program Manager  
Nuclear Waste Program  
State of Washington  
Department of Ecology  
3100 Port of Benton Blvd  
Richland, Washington 99352

Dear Ms. Hedges:

COMPLETION OF HANFORD FEDERAL FACILITY AGREEMENT AND CONSENT  
ORDER (HFFACO) TARGET DATE M-045-91F-T03, DUE MAY 31, 2013

This letter documents completion of the HFFACO target date M-045-91F-T03. This target date requires that the U.S. Department of Energy, Office of River Protection provide to the Washington State Department of Ecology, as a HFFACO secondary document, a report assessing the feasibility of testing for ionic conductivity between the inside and outside of Single-Shell Tanks.

Attached is the Ionic Conductivity Assessment report, RPP-ASMT-51526, which meets the requirements for the target date.

If you have any questions, please contact me, or your staff may contact Thomas W. Fletcher, Assistant Manager for Tank Farms Project at (509) 376-3434.

Sincerely,

A handwritten signature in black ink, appearing to read "Scott L. Samuelson", is written over a horizontal line.

Scott L. Samuelson, Manager  
Office of River Protection

TF: JMJ

Attachment

cc: See Page 2

**MAY 02 2012**

Ms. Jane A. Hedges  
12-TF-0009

-2-

cc w/attach:

S. Harris, CTUIR

J. J. Lyon, Ecology

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Administrative Record

Environmental Portal, LMSI

TPA Administrative Record (S-2-4)


WRPS Correspondence

**ATTACHMENT**

**12-TF-0009**

**IONIC CONDUCTIVITY ASSESSMENT REPORT, RPP-ASMT-51526**

# DOCUMENT RELEASE FORM

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## Tri-Party Agreement Target Milestone M45-91F-T-03 Ionic Conductivity Assessment

**Kayle D Boomer**

Washington River Protection Solutions, LLC

Richland, WA 99352

U.S. Department of Energy Contract DE-AC27-08RV14800

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**Abstract:** To improve DOE's ability to verify the integrity SST liners, Washington River Protection Solutions, LLC (WRPS) investigated the feasibility of using "Ionic Conductivity" to assess tank integrity. The current system (High Resolution Resistivity) measures the decrease in resistance should waste start leaking from a tank. Instead the presence of ions from previous waste leaks would be used to detect ionically-conductive pathways in the tank liners, which would provide an indication of the loss of liner integrity without increasing the amount of waste in the vadose zone. If successful, this technique would allow the integrity determination prior to retrieval operations instead during the operations.

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**APPROVED**

By TIFFANY M PHILLIPS at 3:20 pm, Feb 01, 2012

Release Approval

Date



Release Stamp

**Approved For Public Release**

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1	To comply with Hanford Federal Facility Agreement and Consent Order terminology.	K. D. Boomer	D. J. Washenfelter	
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**TRI-PARTY AGREEMENT TARGET DATE  
M45-91F-T-03  
IONIC CONDUCTIVITY ASSESSMENT**

**January 2012**

**Prepared by:**

**K.D. Boomer**

**Washington River Protection Solutions, LLC  
Richland, Washington**



Washington River Protection Solutions, LLC (WRPS) investigated the feasibility of using "Ionic Conductivity" to assess tank integrity. The current system (High Resolution Resistivity) measures the decrease in resistance should waste start leaking from a tank. Ionic conductivity uses the presence of ions from previous waste leaks to detect ionically-conductive pathways in the tank liners, which would provide an indication of the loss of liner integrity without increasing the amount of waste in the vadose zone. If successful, this technique would allow the integrity determination prior to retrieval operations instead during the operations.

It was determined the initial concept for "Ionic Conductivity" of modeling the Electrochemical Impedance Spectroscopy (EIS) of the leak would not work because the ratio of the area of the liner defect to tank surface would have to be large to detect the presence of the defect. During the course of the testing it was observed that differences in the corrosion potential may provide an alternate method for verifying liner integrity.

The work was part of the M-45-91F milestone series. This milestone and the associated target dates have the overall goal of providing enhanced Leak Detection Monitoring and Mitigation (LDMM) methods. The work for "Ionic Conductivity" was accelerated to support completion of the balance of these milestones during 2012 so that all of the milestones would be completed simultaneously to provide insight for the Tri-Party Agreement members. The specific target date called for:

<u>M-045-91F-T-03</u>	<u>DOE shall provide to Ecology, as a HFFACO secondary document, a report assessing the feasibility of testing for ionic conductivity between the inside and outside of SSTs.</u>	<u>May 31, 2013</u>
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The feasibility study was conducted through the Ohio State University and its supporting laboratory at the Den Norkse Veritas (DNV) facility in Columbus, Ohio. Their study is attached in Appendix A. The work consisted of modeling of the system followed by testing at three scale-up levels: 4-inch diameter can, 6-inch diameter can, and 26-gallon container. The original scope of this work would have been satisfied with just the modeling and bench scale testing in the four and six-inch diameter cans.

The researchers continued on to the larger scale to understand the relationship between defect area and tank area. The approach was shown to be viable for detecting a defect in a small can, but is not suitable for detecting small defects in a large waste container. More specifically, the method should be able to detect a defect with area that is more than about 1000 times smaller than the exposed tank area, but not if the defect area is 10,000 times smaller than the exposed tank area. The final phase of testing supported this conclusion as a small hole in the drum had little influence on the EIS response.

The researchers identified an alternate approach for testing. The approach would use either the corrosion voltage (potential) difference or the potential decay. This approach has not been fully developed, but could become the basis for improved LDMM techniques in the future. The development of this technique could be part of the activities developed for the Enhanced Single-Shell Tank Integrity Project Phase II work to be conducted under the Hanford Facility Federal Agreement and Consent Order (Tri-Party Agreement).



## **Appendix A**

### **Through-Tank Ionic Conductivity Measurement Feasibility Study**

Final Report

## **Through-Tank Ionic Conductivity Measurement Feasibility Study**

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10/6/11

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## Executive Summary

An approach was investigated to detect the presence of ionic-conductive pathways in SST steel liners. An ionic pathway might represent a crack at a level below the waste, which is difficult to detect. The approach uses Electrochemical Impedance Spectroscopy (EIS), in which measurements are made on a working electrode immersed in the waste inside the tank using counter and reference electrodes embedded in the ground outside the tank in the ground. With such an approach, there is no need to make electrical contact to the tank liners.

In the first task an equivalent electrical circuit was developed to simulate the EIS response of the system with and without the presence of a crack. In the second task, bench top experiments were performed using cans embedded in dirt. The measurements were able to detect the presence of cracks intentionally created in the cans and the EIS response was similar in form and magnitude to that predicted by the equivalent circuit developed in Task 1. This validated the model and the values of the parameters used to determine the model circuit element values. However, both the experiments and the simulation modeling predict that the approach will only be able to detect defects such as cracks or holes in the SST steel liner if the area of the defect is relatively large. The reason for this is that the resistance to current flow through the intact part of a can or tank liner decreases as the area increases. Therefore, the approach is viable for detecting a defect in a small can, but is not suitable for detecting small defects in a large waste container. More specifically, the method should be able to detect a defect with area that is more than about 1000 times smaller than the exposed tank area, but not if the defect area is 10,000 times smaller than the exposed tank area. Task 3 (performed on a large 25.6 gal drum) supported this conclusion as a small hole in the drum had little influence on the EIS response.

During the course of the work, a difference in the corrosion potential of the working electrode inside the cans relative to a reference electrode outside the cans was observed for defective cans compared to sound cans. It was shown that the corrosion potential can be a diagnostic indicator of can soundness only if there is a difference in corrosion potential of the can itself in the interior and exterior environments. For the case where this difference in corrosion potential is small, it might be possible to examine the potential decay after interrupting a current between two auxiliary electrodes to sense the presence of a defect.

## Background

High level radioactive waste from defense operations is being stored in carbon steel tanks at the Hanford Site in the State of Washington. Of the 177 tanks, 149 are single shell tanks (SSTs) that consist of non-stress-relieved welded steel liners inside reinforced concrete shells. As many as 67 of the SSTs could have leaked, resulting in the loss of approximately 1 million gallons of waste into the ground. Part or all of the leaks could have been associated with corrosion or stress corrosion cracking of the steel caused by the high temperature, pH, and nitrate ion concentration of the liquid waste. When this corrosion susceptibility became apparent and understood, the tanks were "interim stabilized" by transferring the pumpable liquid from every SST into double shell tanks. The material remaining in the tanks is either a solid precipitate referred to as "saltcake" or a highly viscous liquid/solid composite with the consistency of mud and referred to as "sludge." It was assumed that the radioactive species in these waste forms were much less mobile than the liquid that was pumped out.

The SSTs must eventually be retrieved, i.e. cleaned of all radioactive waste. Detailed procedures for safe removal of saltcake and sludge from tanks that are suspected leakers have not been developed, but sluicing with a water jet is a likely approach. One concern is the possible existence of cracks in the liner, either above or under the current tank content level. There is no evidence that interim stabilized tanks have been leaking. However, existing cracks above the waste level that were formed when the waste was

at a higher level or as the result of vapor space corrosion might leak when the waste is liquefied by the water jet. It is also possible that cracks or through-holes exist at a level below the current contents as the result of attack during early usage or even during interim storage. The relative immobility of the solid waste forms might be preventing detectable amounts of leakage now, but the liquefaction of the waste during sluicing might result in the release of waste into the surrounding soil.

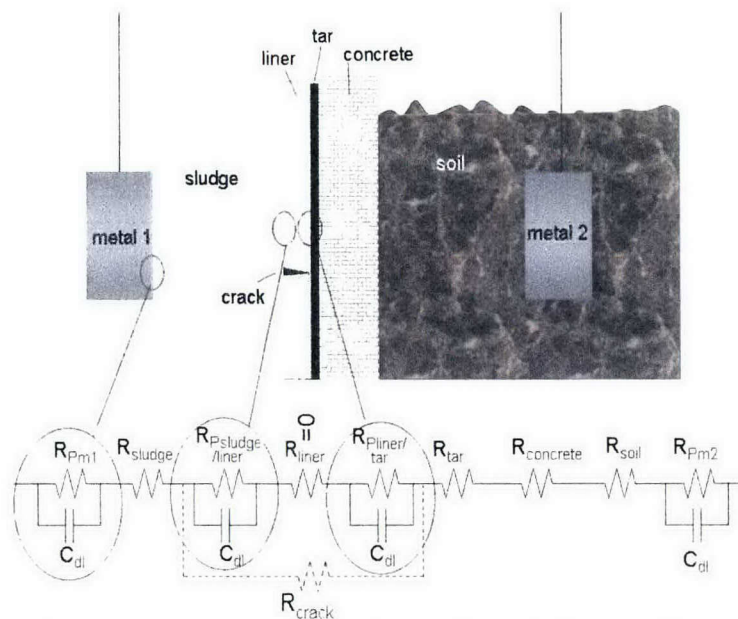
As a result, it is of interest to have knowledge of the existence of any through-liner pathway under the current waste level and to have a sensor system to detect such a pathway above the current waste level if sluicing will increase the waste level. The radioactive species are present in the waste in the form of ions, so a pathway that could lead to radioactive leakage would be one that exhibited ionic conductivity. The goal of this project has been to investigate an approach to detect the presence of ionic-conductive pathways in the SST steel liners.

## Approach

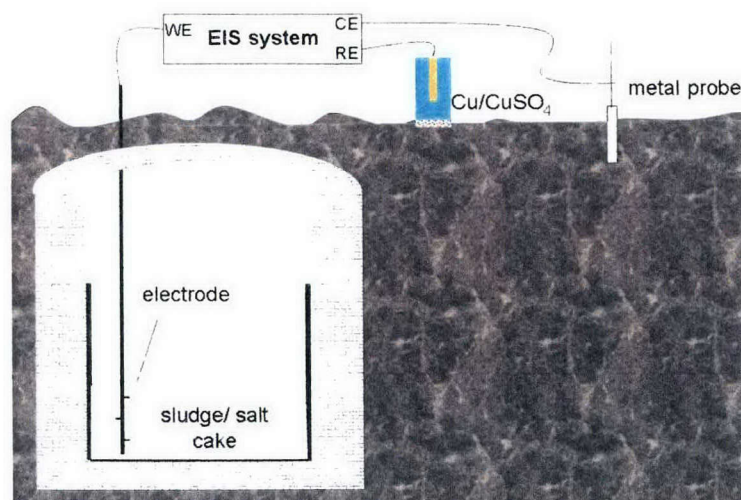
It might be possible to test for ionic conductivity by inserting a probe into the tank sludge layer and another outside of the tank in the ground and measuring the resistance or impedance between the two. Figure 1 and Figure 2 show schematic illustrations of electrodes in and outside of an SST. Between these electrodes are various phases that provide resistance. To measure a resistance, a small current must be passed. Note that electrical current can be carried either by electrons in an electrical conductor such as metal or by ions in an ionic conductor such as sludge, saltcake, or soil. Current can also flow between electronic and ionic conductors as the result of electrochemical reactions at the interface of an electrically-conductive electrode and an ionically-conductive electrolyte.

It is reasonable to assume that a good electrical connection could be made between a metal probe immersed in the tank sludge or saltcake (labeled Metal 1 in Figure 1) and a resistance meter such that the resistance along that connection would be essentially zero. A resistance exists across the metal/sludge interface. In fact, an equivalent electrical circuit consisting of a parallel resistor and capacitor can represent the electrical response of many electrode/electrolyte interfaces. The resistance, called polarization resistance ( $R_p$ ), is inversely proportional to the rate of the electrochemical reaction. If the metal electrode is corroding, then the polarization resistance is a measure of the corrosion rate. The capacitance is associated with the electrical double layer that sets up at this interface and is called the double layer capacitance.

Following the electrical path to the right in Figure 1, the ionic current would flow through the sludge or saltcake (indicated in Figure 1 as sludge for simplicity) until reaching the next barrier, the tank liner. Transport resistance through the sludge can be represented by a resistor, the value of which,  $R_{\text{sludge}}$ , would depend on the resistivity of the sludge and the geometry of the current flow (length and cross-sectional area). Assuming that the tank liner is intact with no ionic pathway connected with a through-crack, the ionic current would have to convert to electrical current at the sludge/liner interface. This interface can be represented by another parallel resistor and capacitor as shown in Figure 1. The electrochemical reaction at this interface (passive dissolution of the tank metal) would convert the ionic current back to an electronic current, which would flow through the tank metal. The resistance associated with this current,  $R_{\text{liner}}$ , would be essentially zero. The current would then be converted back to ionic current at the outer surface of the liner.



**Figure 1: Schematic of a system to measure ionic pathways. Expanded image of the current path segments between a metal electrode in a tank and one in the ground including an equivalent circuit.**



**Figure 2: Schematic of an EIS system to measure ionic pathways.**

The outer liner surface is covered with tar that acts as a sort of water-proofing. The nature of this phase in terms of its electrical and ionic resistance is not clear. However, it is certainly not a perfect water-proofing or else waste would never leak. There is some conductivity of the tar phase,  $R_{tar}$ . The next phase is the concrete, which has a resistivity associated with the pore water, which reaches equilibrium with the calcium hydroxide in the cement. The conductivity of concrete, and the next phase, which is soil, depends on the amount of water available. Both concrete and soil can be quite conductive if enough water is present, which would allow passage of ionic current until reaching the interface associated with the electrode in the soil, Metal 2.

If the liner is breached by a through-wall defect that is ionically-conductive, then it is possible for part of the equivalent circuit in Figure 1 to be shorted. At a minimum the defect would short the two liner interfaces and it might also short the tar layer. If the resistance of the defect were low compared to the



resistances of these interfaces and phases, then the current would flow preferentially as ionic current from the sludge to the concrete (i.e. the path of least resistance). A resistance meter operating in DC mode might sense the difference in resistance between a shorted and sound tank. One would have to use a tank thought to be sound as a control case.

Instead of using a DC resistance measurement, it might be possible to be more sensitive to such defects using an AC measurement such as electrochemical impedance spectroscopy (EIS). EIS would require the use of a third electrode, a reference electrode, placed on the ground between the tank and the auxiliary or counter electrode. In brief, EIS works by applying a potential sine wave of varying frequency to an electrode and measuring the current. One can obtain the impedance as a function of the frequency. The impedance is, in general, a complex number owing to any capacitance in the equivalent circuit describing the electrochemical system. The response of a system with an ionic short through the liner would be different than that of a system having a sound liner with electrochemical interfaces on either side. This would be true if the time constants,  $R \times C$ , of the polarization resistances and double layer capacitances associated with the liner interfaces were vastly different than the time constant of Metal 1 in the sludge. These different time constants would provide an EIS spectrum of very different nature than if there were an ionic path directly from the surface of Metal 1 to the soil.

As a result, the EIS response of an electrode immersed in a tank with reference and counter electrodes placed outside the tank (Figure 2) should provide information about the existence of any through-wall defect in the liner. However, it would only sense defects below the level of the sludge or saltcake. On the other hand, such a technique might be useful during retrieval operations to sense for leaks through cracks above the sludge top surface layer as liquid is sluiced into the tank. If a change in the impedance response were sensed during retrieval, operations could be shut down to prevent leakage.

EIS is a practical technique that has wide application. However, there are several unknowns and possible artifacts that could complicate the measurement. The values of the circuit elements shown in Figure 1 are unknown so that it is not clear if the resistance or impedance of a cracked liner would be different than that of a sound liner. It should be noted the area normalized resistance associated with the polarization resistance of an electrochemical interface has dimensions of  $\Omega\text{-cm}^2$  and the resistance of the full exposed area is determined by dividing this value by the area. For a large tank, this would result in a low resistance. The stray capacitance associated with long lead wires also can create problems with this measurement.

## Summary of Tasks

The project consisted of the following three tasks:

### Task 1. Equivalent Circuit Modeling

It is possible to assemble passive electrical elements such as resistors, capacitors, and inductors into a circuit that responds to voltage stimulation in a fashion similar to real electrochemical systems. Often an imaginary construct called a constant phase element (CPE) is used instead of capacitors owing to the non-ideal capacitive response of many electrochemical systems. The circuit at the bottom of Figure 1 is one such equivalent circuit.

A common approach to testing with EIS is to fit an equivalent circuit to the measured data to extract values of the equivalent circuit elements. In Task 1, the system was model before any experimentation. Estimated values of polarization resistance, double layer capacitance (or CPE element values), resistivity of soil, saltcake, and sludge, and tank geometry were used to construct an equivalent circuit that is thought to represent that of the tank. The circuit shown in Figure 1 was a starting point. Circuit element values representing lab-scale and pilot-scale models were also used. The expected responses of these equivalent circuits to different voltage stimulation were probed using software designed to do this.

The results of Task 1 were used to guide the experimental approaches described below in Tasks 2 and 3.

### Task 2. Lab Bench Scale Testing

Lab bench scale models were constructed using steel coffee cans, which were stripped of any organic layer protection and tinplate, as a tank analog. Two cans with different diameters were used: 4 and 6 in. The waste was modeled using a concentrated high pH nitrate solution similar to the simulants that have been used in the DST testing at DNV. Soil was used outside of the can. Experiments were performed with openings of different sizes machined into the can. Electrochemical measurements were performed to test for sensitivity to the defects. The equivalent circuit model from Task 1 was utilized to compare with the results as a model validation exercise.

### Task 3. Larger Scale Testing

If the results of Tasks 1 and 2 were encouraging, it was planned to perform larger scale tests in the ground outdoors. However, it was winter time when the time came, and it was instead decided to use soil boxes that exist in the basement of the DNV labs. It was originally planned to use a 55 gal drum, but a 25.6 gal drum was used instead. Similar effects of through-defect size and phase conductivities were investigated with different approaches.

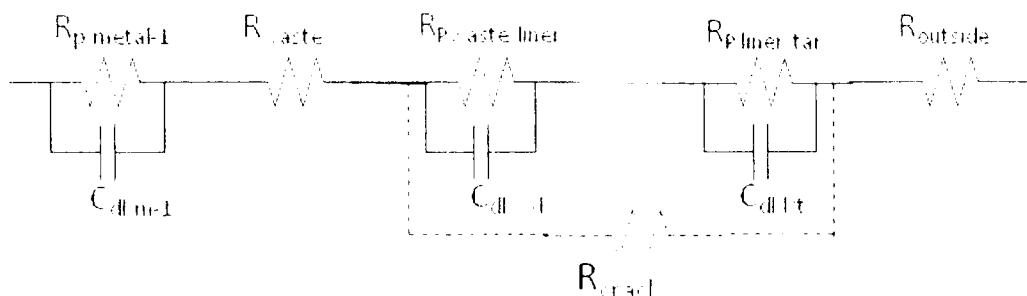
It should be noted that the concrete shell is ignored in these scale models. The assumption here is that the conductivity of the concrete should be better than that of the soil, owing to the high solubility of the calcium hydroxide in the concrete, which results in conductive pore solutions.

## Results and Discussion

The results of the three tasks will now be presented.

### Task 1. Equivalent Circuit Modeling

A modified version of the circuit shown in Figure 1 was used. As shown in Figure 3, several simplifications were made. The resistance associated with the liner was considered to be extremely small and was ignored. For simplicity, the circuit to the right of the liner/tar interface was combined into one resistance,  $R_{outside}$ . Also, note that the term waste is used to represent the contents, which can be sludge and/or salt cake.



**Figure 3:** Equivalent circuit used to model SST.  $R_{p,metal-1}$  and  $C_{dl,metal-1}$  represent the polarization resistance and double layer capacitance of the electrode immersed in the tank.  $R_{p,waste/liner}$  and  $C_{dl,waste/liner}$  represent the polarization resistance and double layer capacitance of the waste/liner interface,  $R_{p,liner/tar}$  and  $C_{dl,liner/tar}$  represent the polarization resistance and double layer capacitance of the liner/tar interface,  $R_{waste}$  represents the resistance of the waste,  $R_{outside}$  represents the impedance of everything outside of the liner, and  $R_{crack}$ , which is only present when modeling cracked tanks, represents the resistance of current flow to and through the crack.

It was realized early on that there is a large resistance associated with the concentration of current from a conductive phase to a small area. This is typically considered for a small circular or rectangular electrode embedded into a non-conductive medium like epoxy. However, it holds for the case of current

flowing from the waste to a crack and then out into the surrounding ground. Therefore, the resistance noted as  $R_{\text{crack}}$  was actually the sum of three resistances: that associated with concentration of current from the waste to the crack, that associated with flow of current through the crack, and that associated with spreading of current from the crack to the outside of the liner. The primary resistance of a rectangular electrode of width  $w$  and height  $h$  in a solution of resistivity  $\rho$  is  $(\rho/2\pi w)\ln(4w/h)$  and the resistance associated with the flow of current through a rectangular slot of width  $w$ , height  $h$ , and length  $l$  is  $\rho l/wh$ . Note for a crack in a liner that  $l$  would be the liner thickness. Therefore, the value used for crack resistance was:

$$R_{\text{crack}} = (\rho_{\text{waste}}/2\pi w)\ln(4w/h) + \rho_{\text{crack}}l/wh + (\rho_{\text{outside}}/2\pi w)\ln(4w/h) \quad (1)$$

where  $\rho_{\text{waste}}$ ,  $\rho_{\text{crack}}$ , and  $\rho_{\text{outside}}$  are the resistivities of the waste, crack and outside region (concrete and soil), respectively. It is assumed that  $\rho_{\text{crack}} = \rho_{\text{waste}}$ .

The resistances associated with the various polarization resistances are  $R_p/A$  where  $A$  is the area of the electrode because polarization resistance has the units of ohm-cm<sup>2</sup>. Therefore, the resistance associated with a large electrode such as a tank is very small for typical values of polarization resistance. As will be shown, this is the limiting factor in the sensitivity of the approach.

The capacities associated with the various double layer capacitances are  $C_{dl}A$  because the capacitance is area normalized in the typical fashion with units of F/cm<sup>2</sup>. As a result, for large area electrodes, the capacity will be very large.

The resistance of the waste was taken as the parallel combination ( $R_1R_2/(R_1+R_2)$ ) of the resistance flow from a central electrode to the side,  $R_1$ , and to the bottom of the liner,  $R_2$ .  $R_1$  and  $R_2$  were estimated as  $\rho_{\text{waste}} \text{radius}_{\text{tank}}/\text{area}_{\text{waste-side}}$  and  $\rho_{\text{waste}} \text{height}_{\text{waste}}/\text{area}_{\text{tank-bottom}}$ , respectively.

The outside resistance was considered to be the sum of the resistance of the concrete and the soil. The resistance of the concrete was taken as  $\rho_{\text{concrete}} \text{thickness}_{\text{concrete}}/\text{area}_{\text{liner-total}}$  and the resistance of the soil was taken as  $\rho_{\text{soil}} \text{distance}_{\text{tank-RE}}/\text{area}_{\text{tank-profile}}$ .

Values used in the equivalent circuit simulation analysis are given in Tables 1 - 3. Table 1 shows the physical properties used in the analysis and Tables 2 and 3 show the values of the equivalent circuit elements calculated from those properties and the above equations. Two levels of waste were considered: 100 and 600 cm. The results with no crack in the tank (a very large value of  $R_{\text{crack}}$  was used in the analysis) were compared to those with a crack of varying dimension, crack width = 1, 10, or 100 cm and crack height = 0.1 or 1 cm. The values of  $R_{\text{crack}}$  for the different combinations of width and height are given in Table 3.

Table 1. Parameter values used for equivalent circuit modeling

Parameter	Value	Parameter	Value
$R_p$ metal l	$100 \Omega\text{-cm}^2$	Liner thickness	0.8 cm
Area metal l (rod of length 1 m and diameter 10 cm)	$3300 \text{ cm}^2$	$R_p$ waste/liner	$1\text{E}6 \Omega\text{-cm}^2$
$C_{dl}$ metal l	$1\text{E-}5 \text{ F/cm}^2$	$R_p$ liner/tar	$1\text{E}7 \Omega\text{-cm}^2$
$\rho_{\text{waste}}$	$10 \Omega\text{-cm}$	Waste side area	$7.2\text{E}5$ or $4.3\text{E}6 \text{ cm}^2$
$\rho_{\text{concrete}}$	$300 \Omega\text{-cm}$	Bottom area	$4\text{E}6 \text{ cm}^2$
$\rho_{\text{soil}}$	$1000 \Omega\text{-cm}$	Liner height	900 cm
Tank diameter	2300 cm	Liner area total	$1\text{E}7 \text{ cm}^2$
Waste height	100 or 600 cm	Liner area profile (diameter x height)	$2.1\text{E}6 \text{ cm}^2$
Concrete thickness	10 cm	Distance tank-RE	1000 cm
Crack width	1, 10, or 100 cm	Crack height	0.1 or 1 cm
$C_{dl}$ , waste/liner	$1\text{E-}6 \text{ F/cm}^2$	$C_{dl}$ , liner/tar	$1\text{E-}6 \text{ F/cm}^2$

Table 2. Equivalent circuit element values.

Element	Value
$R_{p, \text{ metal-1}}$	$3\text{E-}2 \Omega$
$C_{dl, \text{ metal-1}}$	$3.3\text{E-}2 \text{ F}$
$R_{\text{waste}}$	$2.5\text{E-}4$ or $1.2\text{E-}3 \Omega$ (for waste height 100 or 600 cm)
$R_{\text{waste/liner}}$ ( $R_{p, \text{ waste/liner}} = 1\text{E}6 \Omega\text{-cm}^2$ )	$1.4$ or $0.23 \Omega$ (for waste height 100 or 600 cm)
$C_{dl, \text{ waste/liner}}$	$0.72$ or $4.3 \text{ F}$ (for waste height 100 or 600 cm)
$R_{\text{, liner/tar}}$	$1 \Omega$
$C_{dl, \text{ liner/tar}}$	$10 \text{ F}$
$R_{\text{concrete}}$	$3\text{E-}3 \Omega$
$R_{\text{soil}}$	$0.5 \Omega$
$R_{\text{outside}}$	$0.5 \Omega$

Table 3. Values of  $R_{\text{crack}}$ 

		Crack height	
		0.1 cm	1 cm
Crack width	1 cm	$1.1\text{E}3 \Omega$	$77 \Omega$
	10 cm	$1.2\text{E}2 \Omega$	$19 \Omega$
	100 cm	$13 \Omega$	$3.1 \Omega$

The values shown in the previous tables were used along with the ZView® software package to simulate the impedance response of tanks with different heights of waste and different size cracks. The results are given in the following figures. Two figures are shown for each comparison, the Nyquist plots, which are plots of the imaginary vs. the real components of the impedance in the complex plane, and the Bode plots, which show both log of the impedance magnitude and phase angle (linear) vs. the log of the frequency. These plots are two different ways to view the data and both are included for convenience. However, the differences are small, so they are more visible in the Nyquist plots than in the Bode plots, particularly the Bode magnitude plots, which are log-log plots.

Figure 4 shows the case of 100 cm waste height and cracks with height of 1 cm and varying width. Figure 5 shows the case of 100 cm waste height and cracks with height of 0.1 cm and varying width. Figure 6 shows the case of 600 cm waste height and cracks with height of 1 cm and varying width. Figure 7 shows the case of 600 cm waste height and cracks with height of 1 cm and varying width. The differences between the cases with a crack and with no crack are larger for cracks that are larger (larger width and/or height). This is because the resistance associated with the crack decreases as the crack gets larger. The differences are also larger for the case with a smaller waste height. As the waste height increases, the area on the inside exposed to the waste increases and the resistance to current flow through the uncracked part of the tank decreases. This makes it more difficult to see the lower resistance path associated with the crack.

In conclusion, the changes in impedance response associated with the presence of a crack in the tank are finite but small. This suggests that the approach of using EIS to assess the presence of a crack in a SST is unlikely to be sensitive enough for defects as large as  $100 \times 1 \text{ cm}$  in size.



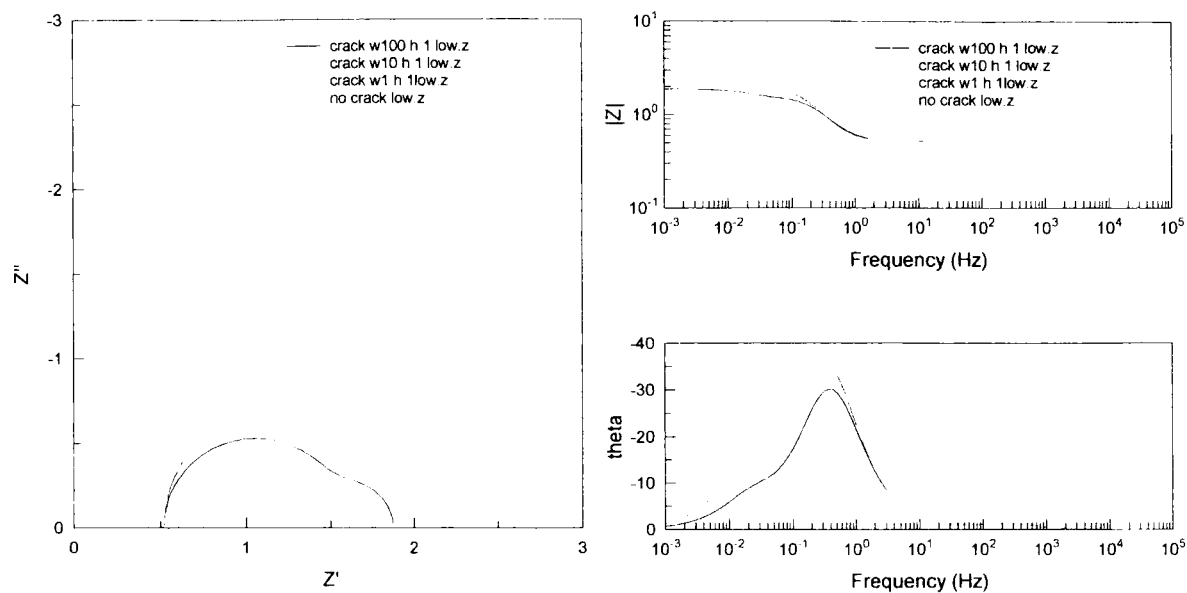


Figure 4: Nyquist and Bode plots for the case of waste height = 100 cm, crack height = 1 cm, varying crack width.

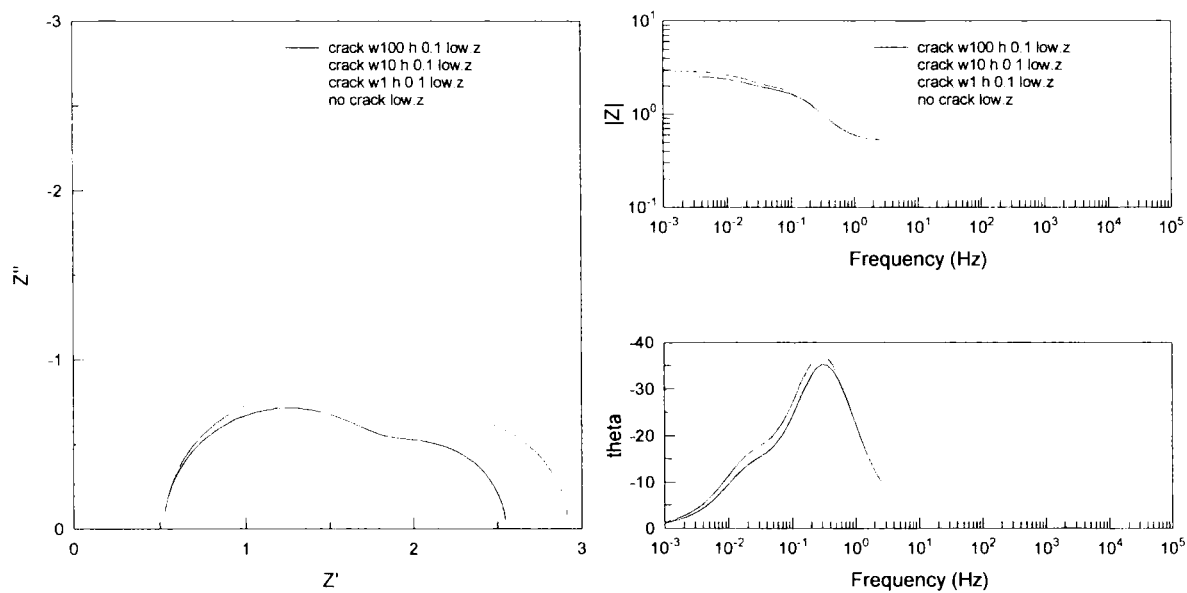


Figure 5: Nyquist and Bode plots for the case of waste height = 100 cm, crack height = 0.1 cm, varying crack width.

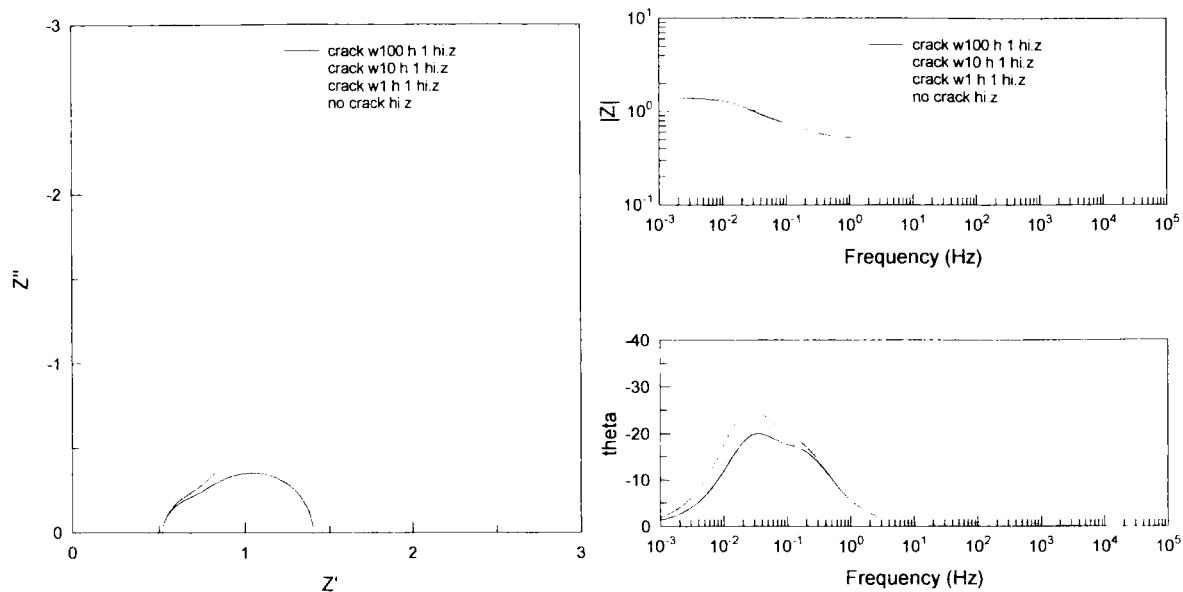


Figure 6: Nyquist and Bode plots for the case of waste height = 600 cm, crack height = 1 cm, varying crack width.

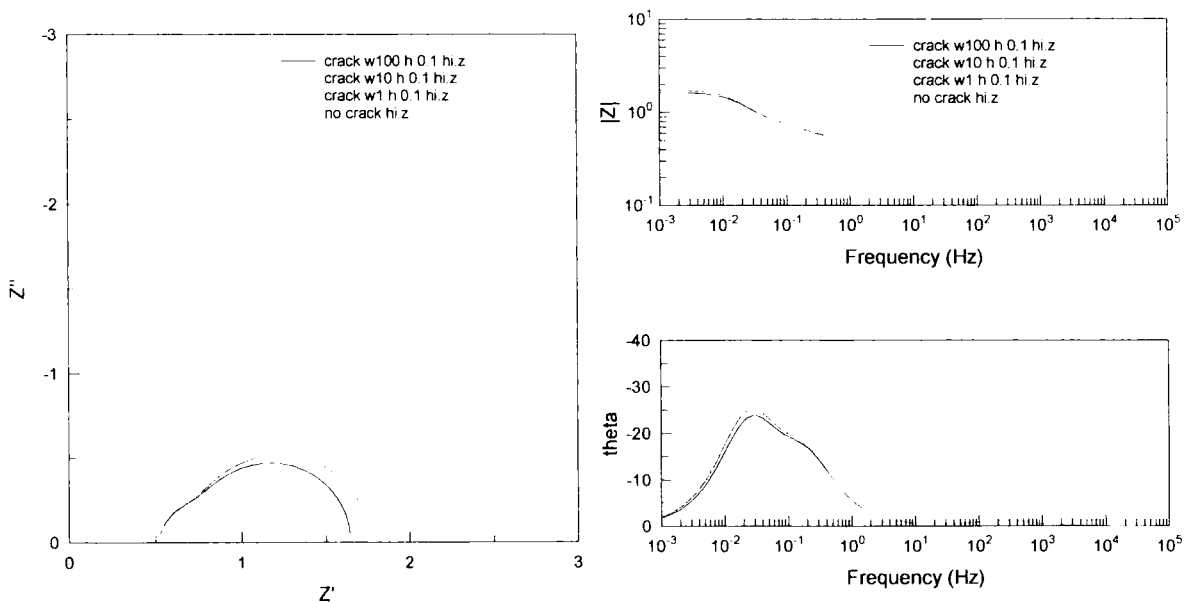


Figure 7: Nyquist and Bode plots for the case of waste height = 600 cm, crack height = 0.1 cm, varying crack width.

### Task 2. Lab Bench Scale Testing

Lab bench scale models were constructed using steel coffee cans as a tank analog. The cans were stripped of any organic layer protection and tinplate by sanding, Figure 8a. Two cans with different diameters were used: 4 and 6 in. The waste was modeled using 5 M  $\text{NaNO}_3$ / 5 M  $\text{NaNO}_2$  solution at pH12, which is similar to the simulants that have been used in the DST testing at DNV. The solution was filled to different levels in the cans.

A 1 mm x 6 cm opening was cut on the can surface using a diamond blade, as can be seen in Figure 8a. Cotton was stuffed into the slot to minimize the loss of electrolyte from the inside of the out into the soil while still maintaining ionic contact, Figure 8b. Twisted Al foil was suspended inside the cans without

touching the sides and was used as working electrode. The cans were embedded in soil contained in a plastic bin, Figure 8c. The soil resistance was measured at 150 ohm-cm. A graphite rod counter electrode and a Cu/Cu<sub>2</sub>SO<sub>4</sub> reference electrode were placed in the soil.

Electrochemical impedance spectroscopy measurements were performed to test for sensitivity to the defects. The equivalent circuit model from Task 1 was utilized to compare to the results as a model validation exercise.

EIS was performed on the Al foil working electrode using a Gamry potentiostat. The can was kept in electrical isolation from the other metal electrodes and the potentiostat. An amplitude of 10 mV was used around the Al foil open circuit potential over a range of frequency from 10<sup>5</sup> to 10<sup>-2</sup> Hz.

Figure 9 shows Bode plots measured for the Al foil working electrode in the can in soil. Figures 9a and 9b are for the 6 in and 4 in diameter cans, respectively. The plots look qualitatively like the plots in Figures 4-7. Figure 10 is the simulated EIS response for the 4 in diameter can using the equivalent circuit in Figure 3 and the same parameters used for simulating the tank in Figures 4-7. The data in Figure 9b are quite close in shape and in magnitude to the simulation in Figure 10. This validates the equivalent circuit in Figure 3 and the parameters in Tables 1-3 used to create Figures 4-7 and supports the conclusions of the modeling in Phase 1.

The responses of these cans with and without cracks are seen to be different, in particular for the smaller can where the low frequency impedance is two orders of magnitude smaller for the cracked can than for the can without a crack. This finding suggests that the method should be useful for detecting cracks. However, as shown in the previous work in Task 1, the area of the can exposed to the waste has a strong influence on the ability of EIS to detect a crack. In the Task 1 analysis, the tank wall to crack area ratio was in the range of 7.3E3 – 4.3E8. The lowest area ratio, for the case of the 100 cm high waste and a crack of dimensions 1 cm x 100 cm shown in Figure 4, was the case that showed the largest effect of a crack. For the 4 in diameter can used in Task 2, the can to crack area ratio was less than 650. This is the reason that the effect of the crack was so large. The effect of the crack in the 6 in can, shown in Figure 9a, was much less because of the higher area ratio.

While the data indicate that the analysis can distinguish a cracked can from a sound can, the approach is shown to be viable only for a small ratio of exposed metal to crack areas.



Figure 8: Images of cans used in Phase 2. a) exterior of 4 in diameter can after cutting slot; b) Slot with cotton stuffed in; c) 6 in diameter can embedded in soil showing reference and counter electrodes in soil; d) 4 in diameter can in soil.

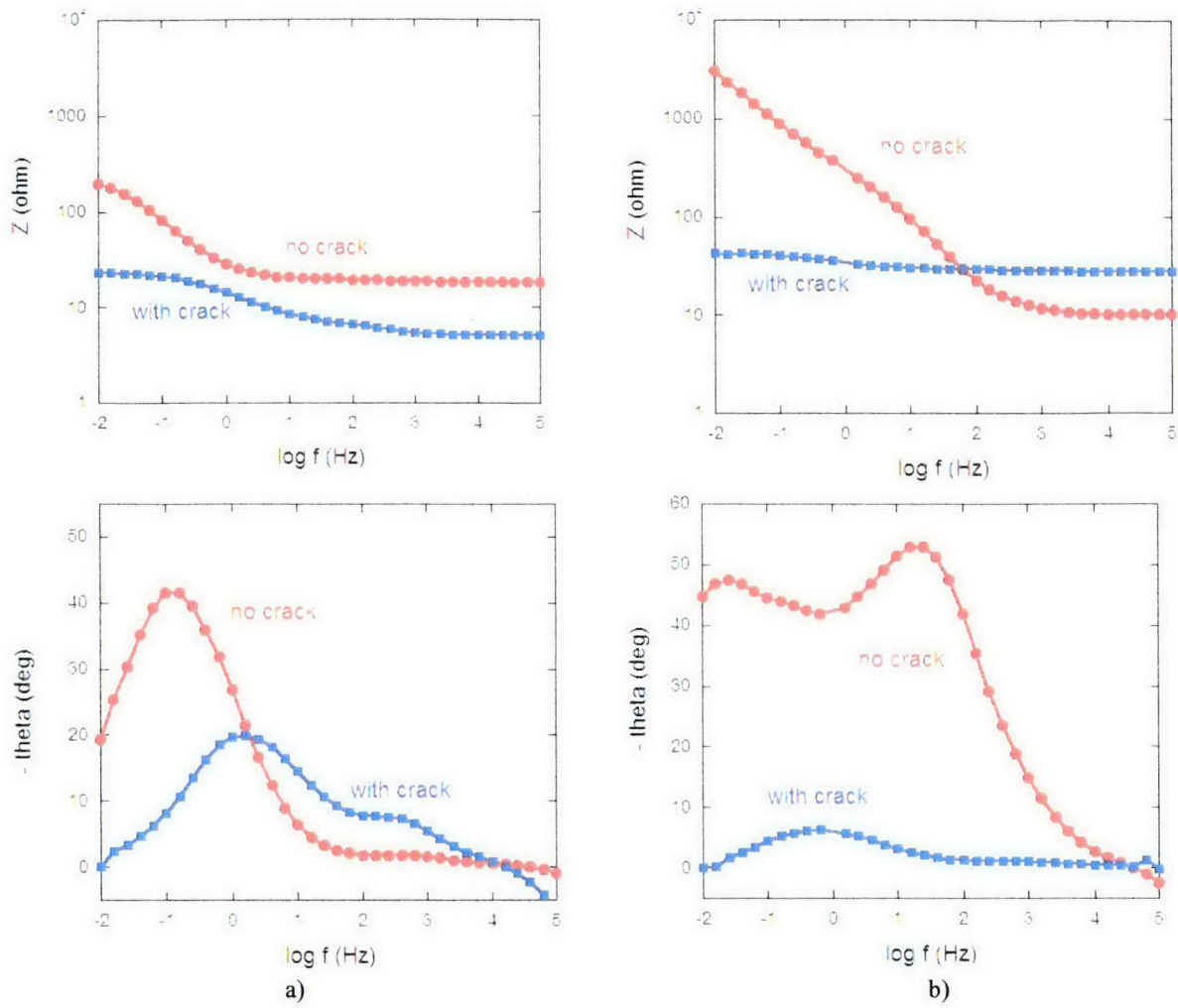


Figure 9: Bode plots of can with no crack and with crack: a) 6 in diameter can; b) 4 in diameter can.



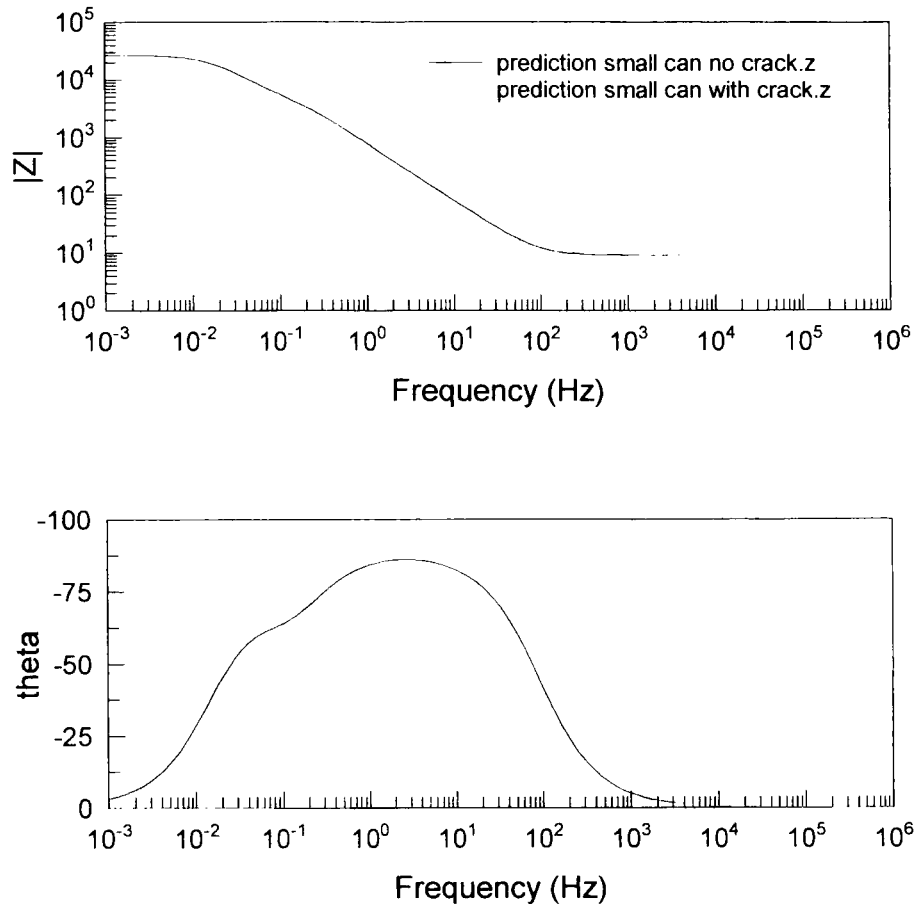


Figure 10: Simulated response of 4 in diameter can using the circuit in Figure 3 and the same parameters used in Phase I except that the values were changed to reflect the smaller can dimensions.

### Task 3. Larger Scale Testing

To further test the effect of area ratio with a yet larger can, a 26 gallon (20 in height by 19 in diameter) can was buried in a soil box in the basement of DNV labs. The dimensions of the soil box were 35 in long (only half of the length was used, the total was 70 in) by 21 in wide by 24 in deep, which contained 10.2 cubic feet of soil. Images of the large can and soil box and large can are shown in Figure 11. It was determined that using a soil box instead of burying the can outside was advantageous because it gave better control over moisture/soil resistivity and it was easier to prevent contaminants (rain water, dust, etc.) from entering the can. The resistance of the soil in the soil box was measured using a Nilsson Soil Resistance Meter (Model 400) and was found to be 1400 to 1700 ohm-cm, which is higher than the resistance of the soil used in Phase 2.

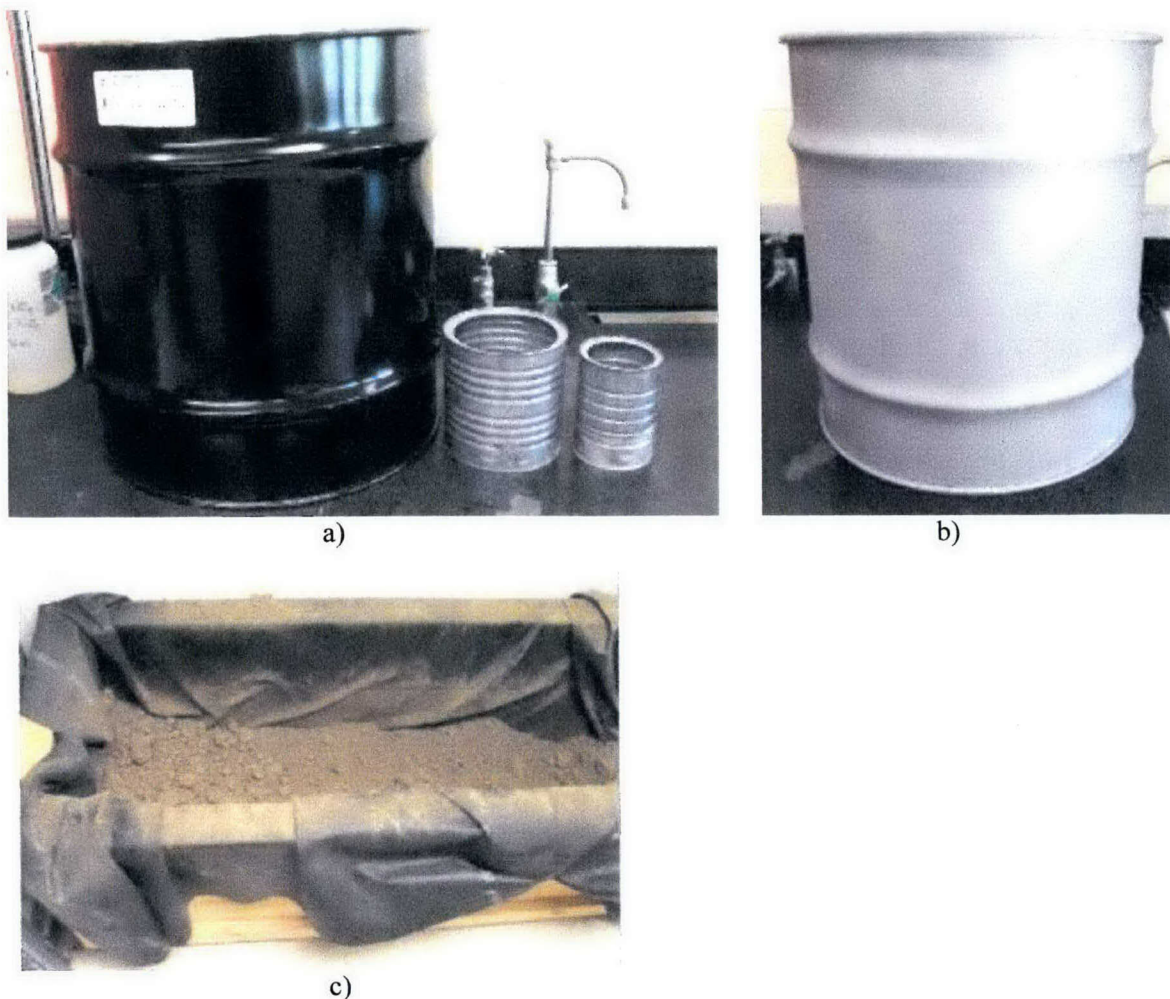


Figure 11: Images of setup in Phase 3; a) 26 gal can tested in Phase 3 next to cans tested in Phase 2; b) 26 gal can after sand blasting; c) soil box used for large can testing.

The coatings on the outside and inside of the large drum were stripped to expose the carbon steel surfaces by sand blasting using 60 grit aluminum oxide media. The solution chemistry was changed for these tests from 5 M  $\text{NaNO}_3$  + 5 M  $\text{NaNO}_2$  solution at pH 12 to 1 M  $\text{NaNO}_3$  + 1 M  $\text{NaNO}_2$  at pH 12 to reduce the amount of chemicals required for solution preparation. EIS tests were conducted on the medium can with this new chemistry to verify that the transition to the new chemistry did not significantly alter the results.

For all tests the surface area of the Al foil working electrode was approximately 65 - 70 in<sup>2</sup>. The counter electrode, a graphite rod of diameter 0.75 in and length 8 in, was buried in the soil 6 in from the can. The Cu-CuSO<sub>4</sub> reference electrode was positioned 3 in from the can. EIS measurements were performed with this configuration at the Al foil OCP using a 10 mV amplitude signal and frequencies from 10<sup>5</sup> - 0.01 Hz.

Experiments were performed with different liquid levels in the can (10 L, 20 L, 40 L, or 80 L, corresponding to 1/8, 1/4, 1/2, and completely full) using a sound can (no defects) and the can with a small hole (1/16 in diameter, 0.00307 in<sup>2</sup> area). The hole was positioned close to the bottom of the can. The can was buried in the sound state and tested. Then the hole was created while the can remained buried using a 1/16" drill bit. The hole location was on the side of the can where the counter and reference

electrodes were situated. The hole was sealed with Hardman® DOUBLE/BUBBLE Extra-Fast Set epoxy to reuse the can for replicate experiments. After creation of the hole, the can was allowed to leak for 12 h and then the foil was inserted and testing was initiated.

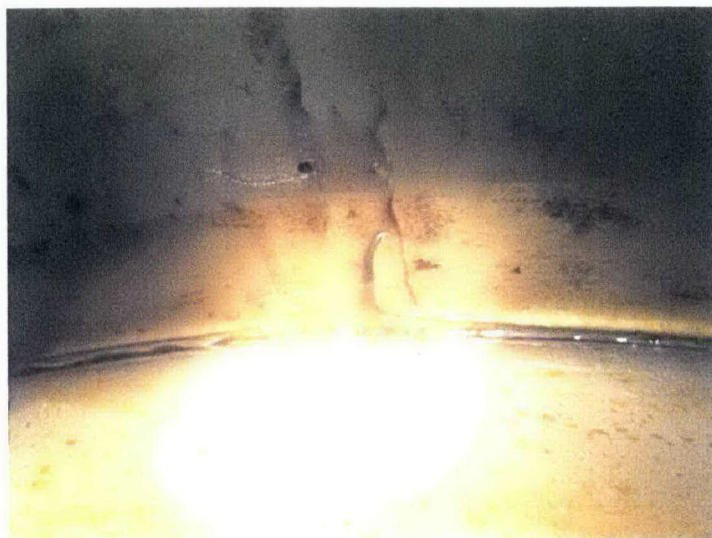


Figure 12: Image of the hole created in the 26 gal can. This picture was taken after epoxy was applied to cover the hole for repeated sound can testing.

In addition to EIS measurements, current interrupt measurements were made with the large can, both with and without the defects. All current interrupt tests were conducted with 40 L of solution in the can (approximately  $\frac{1}{2}$  full). A schematic and picture of the set-up are shown in Figure 13. A power supply was connected between the graphite electrode (mentioned above) positioned in the soil and a Pt-Nb electrode (2.5 in x 0.75 in) positioned in the large can in the 1 M  $\text{NaNO}_3$  + 1 M  $\text{NaNO}_2$  solution. A current of 10 mA was applied between these electrodes. The potential between the Al and  $\text{Cu/CuSO}_4$  reference electrode before and after interruption of the current between the other two electrodes was collected at an acquisition rate of 60 Hz. The current was turned on and the potential of the Al foil WE vs. the  $\text{Cu/CuSO}_4$  RE was monitored until it was stable. The current was then interrupted by disconnecting the lead attached to the power supply and the potential between the Al foil and the  $\text{Cu-CuSO}_4$  reference electrode was recorded for 10 seconds.



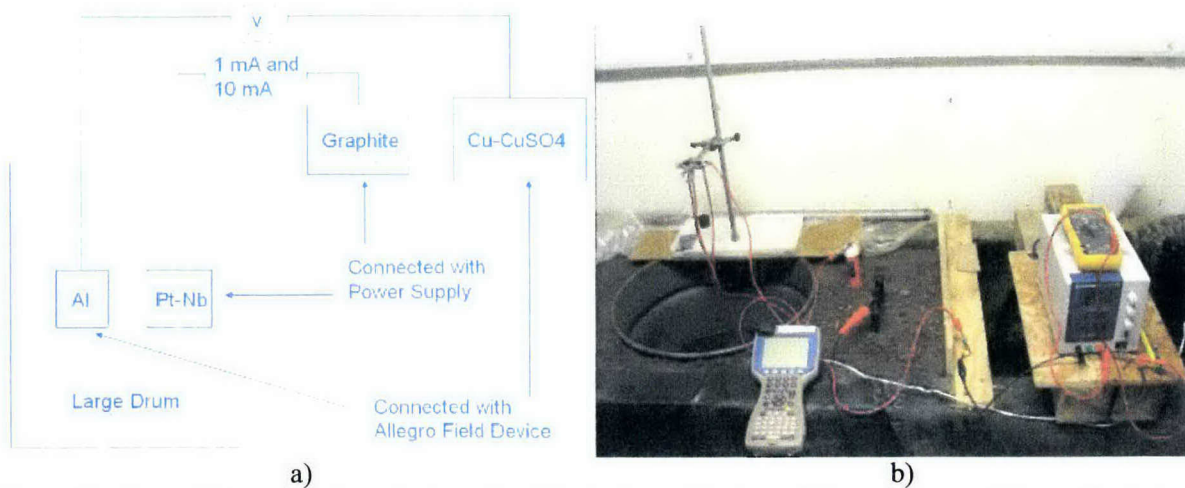


Figure 13: Current interrupt testing; a) schematic of electrodes and devices; b) image of current interruption test set-up.

The results of EIS testing using the drum are shown in Figure 14. These experiments were performed with the drum half full, 40 L. As expected based on the results of the modeling in Task 1 and the experiments in Task 2, little difference was found between the EIS results for the sound can and the can with a hole. Under the test conditions, the exposed drum area was about  $5.7\text{E}3\text{ cm}^2$  and the hole area was about  $2\text{E}-2\text{ cm}^2$ , with a drum/defect area ratio of close to  $3\text{E}5$ . The modeling showed that EIS differences would be extremely small for such a high area ratio. Actually, the results from the testing show that the impedance in the can with the hole is somewhat higher than in the sound can as a result of a higher solution resistance, which is seen at high frequencies.

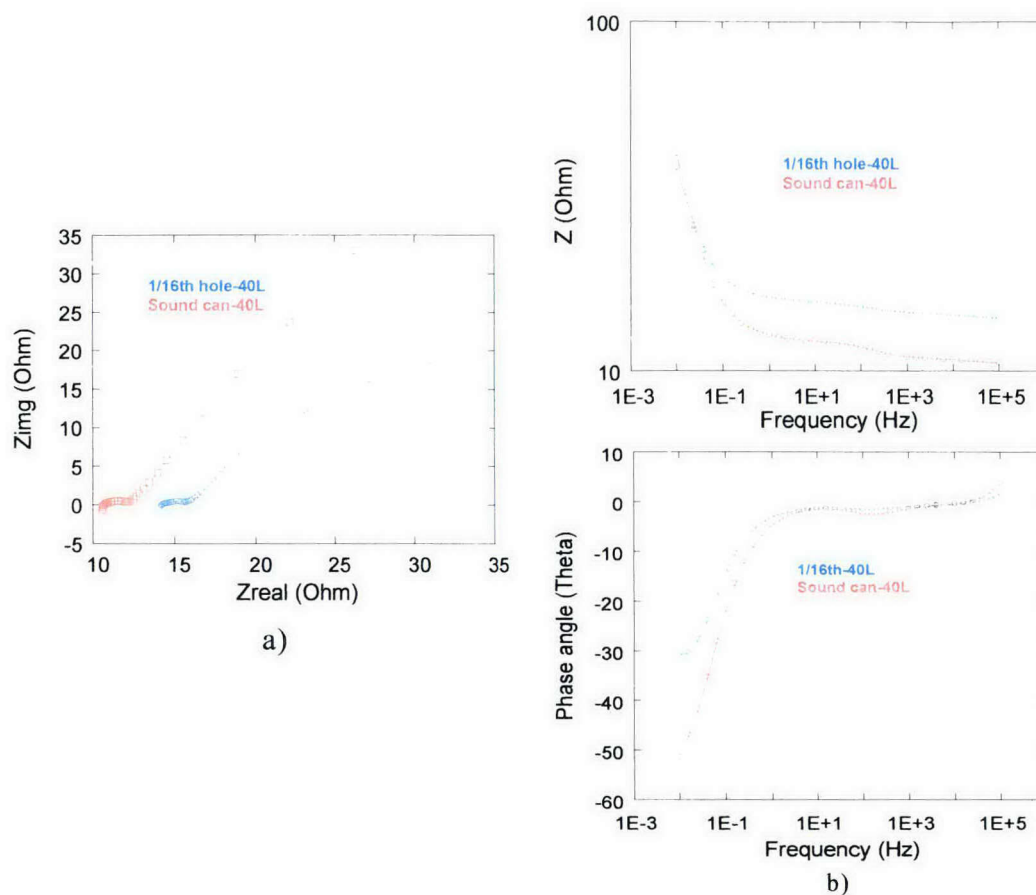


Figure 14: EIS results on sound drum and drum with a small hole: a) Nyquist plot; b) Bode plots.

During the course of this testing, it was noticed that the OCP of the Al working electrode was different for the sound drum and the drum with a hole. It is important to note that the OCP of the Al working electrode inside the drum was measured against a reference electrode located outside of the drum. For a sound can/drum/tank, the OCP measured between an electrode on the inside and a reference electrode on the outside will include two extra potential drops compared with that of a can with a hole. Figure 15 shows a schematic representation of the potential drops in the pathway. There is a potential drop at the interface of the Al working electrode and the waste representing the situation at the Al surface under OCP conditions. This is shown as a sloped line adjacent to the working electrode in Figure 15b. The potential measured against a reference electrode (the OCP or  $E_{corr}$ ) also involves the potential drop across the reference electrode, which is shown as a sloped line next to the reference electrode in Figure 15b. Figure 15b represents the situation where there is a hole in the tank or can. The potential components would be the same if the working electrode were measured against a reference electrode in the waste in the can. If a high impedance voltmeter is used, no potential drop would exist between the working electrode and reference electrode in either case, and the measured value of OCP or  $E_{corr}$  would be the difference between the back ends of the potential drops across the working electrode /solution and reference electrode /solution interfaces and is shown in the figure.



For the case where the working electrode and reference electrode are separated by a sound metal container such as the tank liner or a can wall, two more potential components must be considered. On the inside and outside interfaces of the metal container (interfaces with the waste and concrete, respectively, for a SST), there will be potential drops associated with the respective OCPs in those environments. This is shown schematically in Figure 15c for the case where the two OCPs (inside and outside) are different. The difference in the two OCPs will be added to the total potential difference measured between the reference electrode and working electrode as shown in Figure 15c. This schematic representation explains why the OCP of the Al working electrode was different for a sound drum and the drum with a hole, and suggests that a simple OCP measurement between an electrode in the waste and a reference electrode in the soil could be a diagnostic indicator of the presence of a hole.

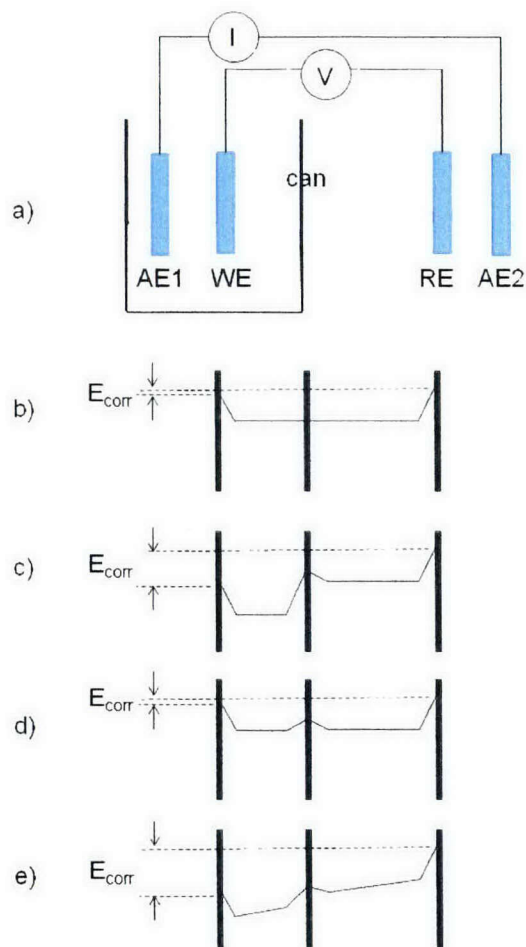


Figure 15: Schematic representations of potential measurement approach: a) layout of electrodes inside and outside of can; WE = Al working electrode inside can, RE = reference electrode outside can, AE1 = auxiliary electrode inside can, AE2 = auxiliary electrode outside can, V = high impedance voltmeter, I = current supply; b) potential components between RE and WE for case where there is a hole in the can or tank (not applied current); c) potential components between RE and WE for case with hole and potential drops on the inside and outside of the can are not the same; d) potential components between RE and WE for case with no hole but the potential drops on the inside and outside of the can are the same; e) potential components when current applied between AE1 and AE2.

This use of working electrode OCP to sense a hole will depend on there being a difference in OCP at the inside and outside of the tank. However, the two environments for an SST could be similar as both will be very alkaline. The environment in contact with the tank concrete is likely one in equilibrium with the

$\text{Ca}(\text{OH})_2$  in concrete and is usually around 13. As pH is a large determining factor for OCP, the inside and outside OCP might be quite close. Figure 15d shows the potential component situation for the case where the tank is sound but the inside and outside OCP values are similar. The working electrode OCP value would be unchanged from the case with a hole and the potential measurement would not be a diagnostic indicator of the presence of a hole. If it were possible to make a connection to the tank liner, one could measure the potential vs. reference electrodes situated inside and outside the tank to know the difference. However, making such a connection is not easy, and one of the advantages of the techniques described in this report is that there is no need to connect to the tank liner.

It might be possible to overcome the problems associated with unknown difference of the inside/outside potential by using two other electrodes to pass a current. Figure 15a shows how a current supply could be used to pass a current between two auxiliary electrodes located inside and outside the tank, respectively. The current would pass through tank, polarizing the inside and outside interfaces. This is represented in Figure 15e by changes in the sloped regions next to the can relative to the case shown in Figure 15d. There would also be an ohmic potential drop in the waste and soil owing to the current flow so the potential lines between the electrodes are sloped in Figure 15e. The corrosion potential under this condition thus has many components, including the ohmic potential drop, which complicates its analysis. However, if the applied current is interrupted, the ohmic potential drops vanish instantaneously, and the potential drops across the interfaces decay with time because of the capacitance of the interfaces. For the case of a tank with a defect, the current would flow through the defect and there would be no capacitive decay, because only ohmic potential drop would exist between the working and reference electrodes. It is possible that analysis of the potential after interruption will provide information about the soundness of the can/tank.

Figure 16 shows the results of the potential measurements. The corrosion potential of the Al working electrode is shown as a function of time for the sound drum and for the drum with a hole. The first values of potential are the OCP with no applied current in the system. There is a clear difference in potential of about 110 mV for the two cases. This difference in the two cases is the result of a different corrosion potential for the inside and outside of the sound drum. The increase in potential observed at about 3000 s is associated with turning on the current between the two auxiliary electrodes. As described above, the current both polarizes the can interfaces and causes an ohmic potential drop in the soil and solution, all of which results in a change in the measured OCP of the working electrode for both cases. The potential for the case with the hole increases by about 275 mV; whereas, for the case of the sound drum, the potential increases by about 300 mV. As the current is turned off at about 4500 s, the potential drops suddenly and then decays back to a value similar to the original OCP. The decay is slower for the sound drum than for the drum with a hole.

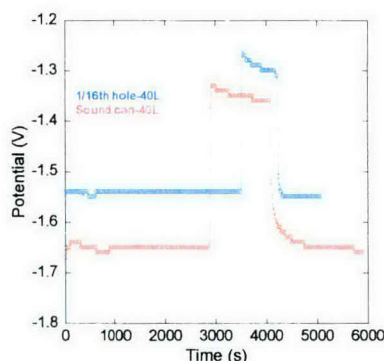


Figure 16: Measured corrosion potential of the Al WE inside the drum vs. the RE located in the soil for a sound drum and for a drum with a hole. During the period from about 3000-4500 s, a current was passed between two auxiliary electrodes located inside and outside the drum.

## Conclusions

This project investigated approaches to sense a breach in an SST liner using electrochemistry. The main approach was to use Electrochemical Impedance Spectroscopy with the working electrode inside the tank and the counter and reference electrodes outside the tank. Equivalent circuit modeling and testing with various scale mock-ups were performed. The EIS approach was found to be suitable for detecting a hole, crack, or other through-wall defect only if the size of the defect was not a very small fraction of the internal area of the tank exposed to waste. Specifically, a defect could be detected if the (tank area)/(defect area) ratio was 1000 or smaller, but not if it was 100,000.

The corrosion or open circuit potential of the working electrode inside the tank relative to an external counter electrode was found to be different for a can with a defect compared with a sound can. This difference, which is the result of a difference in the corrosion potential of the can in the interior and exterior environments, can be used as a diagnostic assessment for the presence of a defect. The potential of an electrode relative to a reference electrode located inside a tank could be compared with the potential relative to a reference electrode outside the tank. If there were differences (accounting for any difference in the reference electrodes), it would indicate that the tank is sound. However, in the case where the interior and exterior tank liner corrosion potential is similar, a false positive is possible. In other words, the corrosion potential of the working electrode would be similar relative to the two reference electrodes even though there was no through-defect in the tank. In this regard it would be a conservative measure.

A current interrupt approach was investigated to deal with the situation of similar interior and exterior potentials. In practice, this approach should work. A difference in the potential decay after current interruption should be evident. However, this approach requires more effort to develop a full understanding and make it viable.